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(54) **Gamma radiation resistant polycarbonate composition.**

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(73) Proprietor: **Bayer Corporation**
One Mellon Center
500 Grant Street
Pittsburgh, PA 15219-2502 (US)

(72) Inventor: **Lundy, Charles E. c/o Mobay Corporation**
Mobay Road
Pittsburgh PA 15 205 (US)
Inventor: **White, Roger J.**
2663 Sunnyfield Drive
Pittsburgh PA 15205 (US)
Inventor: **Krishnan, Sivaram**
1653 Little Meadow Road
Pittsburgh PA 15205 (US)

(74) Representative: **Gremm, Joachim, Dr. et al**
Bayer AG
Konzernzentrale RP
Patente Konzern
D-51368 Leverkusen (DE)

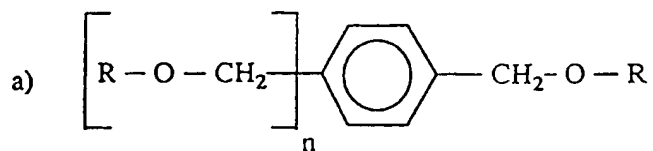
EP 0 384 110 B1

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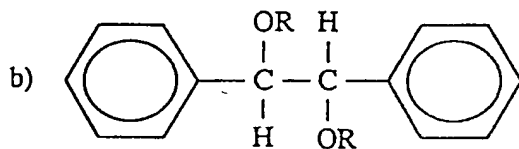
Description

The instant invention is directed to a polycarbonate molding composition comprising a homogeneous blend of

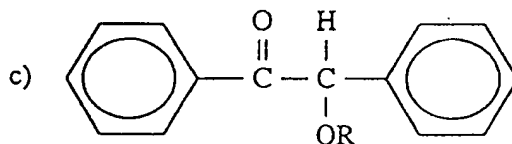
- 5 (i) aromatic polycarbonate resin and
 (ii) 0.01 to 5.0 percent, relative to the weight of said composition, of a member selected from the group consisting of



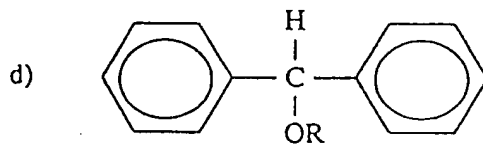
15 wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative and n is 0 or 1,



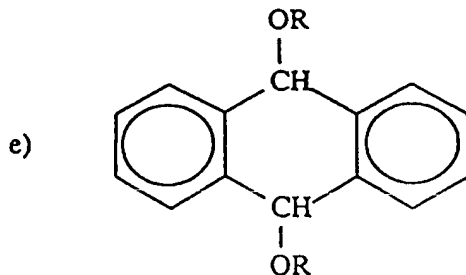
25 wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



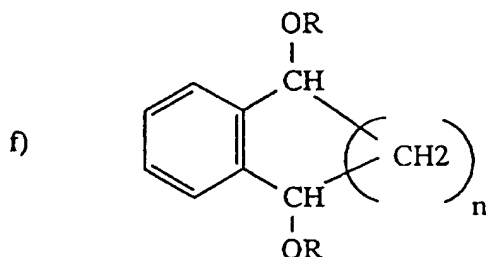
35 wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



45 wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,
and



15 wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative and
n is 1 to 3.

The instant invention is also directed to a molded article prepared from the composition of the
invention.

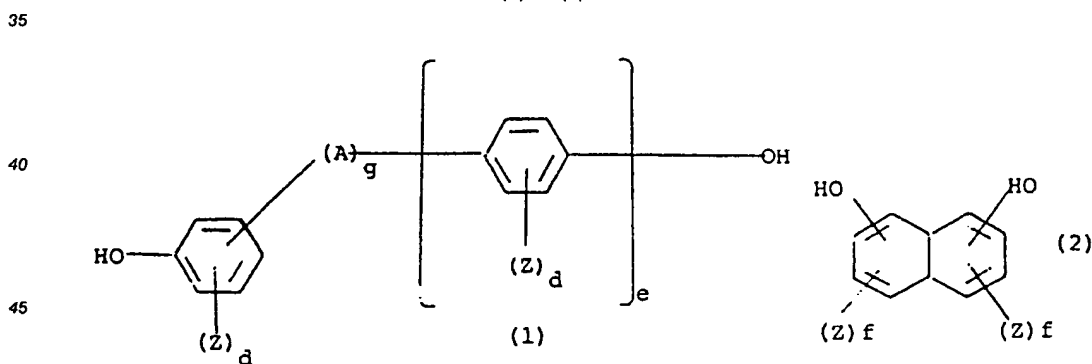
20 The instant invention is neither anticipated by nor obvious over the closest prior art, namely EP-A-0 152
012.

Most preferably R denotes a derivative of dihydropyran which includes tetrahydropyran radicals.

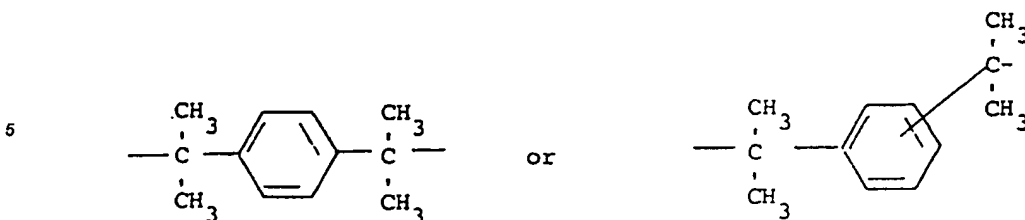
Preferably, the composition contains 0.01 to 1 percent of the stabilizing agent, said percent being
relative to the weight of the composition.

25 The polycarbonate resins useful in the practice of the invention are homopolycarbonates, copolycar-
bonates and terpolycarbonates or mixtures thereof. The polycarbonates generally have a weight average
molecular weight of 10,000-200,000, preferably 20,000-80,000 and their melt flow rate, per ASTM D-1238 at
300°C, is about 1 to about 65 gm/10 min., preferably about 2-15 gm/10 min. They may be prepared, for
example, by the known diphasic interface process from a carbonic acid derivative such as phosgene and
dihydroxy compounds by polycondensation (see German Offenlegungsschriften 2,063,050; 2,063,052;
30 1,570,703; 2,211,956; 2,211,957 and 2,248,817; French Patent 1,561,518; and the monograph H. Schnell,
"Chemistry and Physics of Polycarbonates", Interscience Publishers, New York, 1964, all incorporated
herein by reference).

In the present context, dihydroxy compounds suitable for the preparation of the polycarbonates of the
invention conform to the structural formulae (1) or (2)



50 wherein A denotes an alkylene group with 1 to 8 carbon atoms, an alkylidene group with 2 to 8 carbon
atoms, a cycloalkylene group with 5 to 15 carbon atoms, a cycloalkylidene group with 5 to 15 carbon
atoms, a carbonyl group, an oxygen atom, a sulfur atom, -SO- or -SO₂- or a radical conforming to



e and g both denote the number 0 to 1;

Z denotes F, Cl, Br or C₁-C₄-alkyl and if several Z radicals are substituents in one aryl radical, they may be identical or different one from the other;

d denotes an integer of from 0 to 4; and

15 f denotes an integer of from 0 to 3.

Among the dihydroxy compounds useful in the practice of the invention are hydroquinone, resorcinol, bis-(hydroxyphenyl) alkanes, bis-(hydroxyphenyl) ethers, bis-(hydroxyphenyl)-ketones, bis-(hydroxyphenyl)-sulfoxides, bis-(hydroxyphenyl)-sulfides, bis-(hydroxyphenyl)-sulfones, and α,α' -bis-(hydroxyphenyl)-diisopropyl-benzenes, as well as their nuclear-alkylated compounds. These and further suitable aromatic dihydroxy compounds are described, for example, in U.S. Patents 3,028,356; 2,999,835; 3,148,172; 2,991,273; 3,271,367; and 2,999,846, all incorporated herein by reference. Further examples of suitable bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A), 2,4-bis-(4-hydroxyphenyl)-2-methyl-butane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α' -bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfide, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, hydroxybenzophenone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane, α,α' -bis-(3,5-dimethyl-4-hydroxyphenyl)-p-diisopropylbenzene and 4,4'-sulfonyl diphenol.

Examples of particularly preferred aromatic bisphenols are 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

The most preferred bisphenol is 2,2-bis-(4-hydroxyphenyl)-propane (bisphenol A).

The polycarbonates of the invention may entail in their structure units derived from one or more of the suitable bisphenols.

Among the resins suitable in the practice of the invention are included phenolphthalein-based polycarbonate, copolycarbonates and terpolycarbonates such as are described in U.S. Patents 3,036,036 and 4,210,741, both incorporated by reference herein.

The polycarbonates of the invention may also be branched by condensing therein small quantities, e.g., 0.05-2.0 mol % (relative to the bisphenols) of polyhydroxyl compound. Polycarbonates of this type have been described, for example, in German Offenlegungsschriften 1,570,533; 2,116,974 and 2,113,374; British Patents 885,442 and 1,079,821 and U.S. Patent 3,544,514. The following are some examples of polyhydroxyl compounds which may be used for this purpose: phloroglucinol; 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane; 1,3,5-tri-(4-hydroxyphenyl)-benzene; 1,1,1-tri-(4-hydroxyphenyl)-ethane; tri-(4-hydroxyphenyl)-phenylmethane; 2,2-bis-[4,4-(4,4'-dihydroxy-diphenyl)-cyclohexyl]-propane; 2,4-bis-(4-hydroxy-1-isopropylidene)-phenol; 2,6-bis-(2'-dihydroxy-5'-methylbenzyl)-4-methylphenol; 2,4-di-hydroxybenzoic acid; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane and 1,4-bis-(4,4'-dihydroxy-triphenylmethyl)-benzene. Some of the other polyfunctional compounds are 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

In addition to the polycondensation process mentioned above, other processes for the preparation of the polycarbonates of the invention are polycondensation in a homogeneous phase and transesterification. The suitable processes are disclosed in the incorporated herein by references U.S. Patents 3,028,365; 2,999,846; 3,153,008; and 2,991,273.

The preferred process for the preparation of polycarbonates is the interfacial polycondensation process.

Other methods of synthesis in forming the polycarbonates of the invention such as disclosed in U.S. Patent 3,912,688, incorporated herein by reference, may be used.

Suitable polycarbonate resins are available in commerce, for instance as Makrolon® FCR. Makrolon® 2600, Makrolon® 2800 and Makrolon® 3100, all of which are bisphenol A based homopolycarbonate resins differing in terms of their respective molecular weights and characterized in that their melt flow indices (MFR) per ASTM D-1238 are about 16.5-24, 9-14, 7.5-13.0 and 3.5-6.5 gm/10 min., respectively. These are

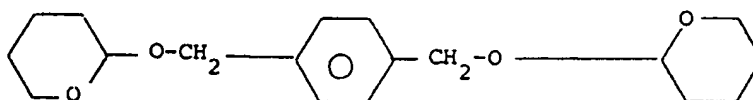
products of Mobay Corporation of Pittsburgh, Pennsylvania, now Miles Inc..

In accordance with the practice of the present invention, a thermoplastic molding composition comprising a polycarbonate resin and an amount of a stabilizing agent is prepared by mixing the agent in the resin to obtain a homogeneous blend. The composition is suitable for the preparation of molded articles. These articles, primarily ones having applicability in the medical field and thus requiring periodic sterilization by exposure to gamma radiation, are characterized by their improved resistance to yellowness and haze which are typically induced in polycarbonate made articles upon their sterilization by exposure to gamma radiation.

The incorporation of the stabilizer in the composition of the invention is carried out following conventional procedures and means well known in the art. The stabilizing agent of the invention may be introduced in the polycarbonate matrix by direct mixing with the resin or by introducing it to the reaction vessel during the production of the polycarbonate resin.

Other conventional additives may also be incorporated in the composition for their art recognized utilities. These additives include release agents, plasticizers, stabilizers, antioxidants, fillers, reinforcements and the like.

The stabilizer of the invention may be readily synthesized following conventional, procedures. The example set forth below demonstrates the preparation of a stabilizer conforming to



In the following examples all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Several compositions stabilized in accordance with the invention were prepared and test specimens were molded therefrom. The specimens were then evaluated to determine their yellowness index in accordance with ASTM 1925-70. The test specimens were then exposed to gamma radiation and their yellowness index determined three days after exposure to the indicated radiation dosage; prior to the determination, the samples were stored in the dark. The table below summarizes the results of the evaluation.

TABLE 1

Type of Added Stabilizer	Amount of Added Stabilizer (%)	Yellowness Index After Exposure to Gamma Radiation		
		0.0	3.5 Mrads	5.0 Mrads
Control	0.0	3.64	22.15	42.91
Hydrobenzoin tetra- hydroxyranyl ether (1)	1.0	3.16	11.20	16.19
Benzoin tetra- hydroxyranyl ether (2)	1.0	6.78	13.73	19.89

(1) Conforming to compound (b) above wherein R is a derivative of dihydroxyran.

(2) Conforming to formula (c) above wherein R is a dihydroxyran derivative.

In all the experiments described above, the polycarbonate used for the preparation of the test specimens was Makrolon® 2608 resin which is a homopolycarbonate based on bisphenol A, having a melt flow index of 9-14 gm/10 min. Makrolon resins are commercial products of Mobay Corporation, now Miles Inc..

EXAMPLE 2

Preparation of an end-capped benzene dimethanol (dihydropyran end-capping): 1,4-Benzene dimethanol (50 g) was dissolved into 600 ml of acetone in a three-necked flask equipped with a stirring apparatus, condenser, dropping funnel, and nitrogen purge. After dissolving the mixture at 40°C, 0.1 g of toluene sulfonic acid was added, then dihydropyran (75 g) was added dropwise over a 1 hour period. After four hours reaction and cooling, triethyl amine (0.07 g) was added. After filtration, the solution was stripped of solvent. The resulting product was a clear slightly yellow liquid.

EXAMPLE 3

The end-capped agent thus prepared was incorporated in a polycarbonate resin and specimens were molded from the composition. The specimens were subjected to gamma radiation, the change in yellowness index was measured and the results are reported below. The effect of the radiation was determined on specimens which were injection molded at 550°F (Melt temperature).

In all the experiments noted below, the polycarbonate was, a bisphenol-A based polycarbonate resin having a melt flow rate of about 19 g/10 min per ASTM D-1238.

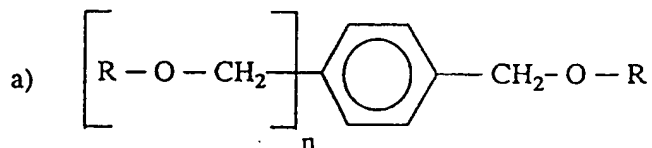
Yellowness Index After Exposure to Gamma Radiation			
Composition	0.0 Mrads	3.5 Mrads	5.0 Mrads
Control ⁽¹⁾ , no stabilizer	3.35	13.05	26.31
1% added benzene dimethanol tetrahydropyranyl ether ⁽²⁾	3.52	5.79	8.06

(1) Makrolon® 2608, a bisphenol A based homopolycarbonate

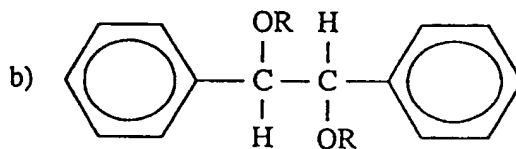
(2) A bis-tetrahydropyran terminated benzene dimethanol

Claims

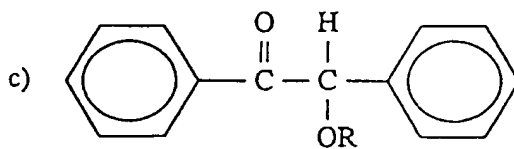
1. A polycarbonate molding composition comprising a homogeneous blend of
 - (i) aromatic polycarbonate resin and
 - (ii) 0.01 to 5.0 percent, relative to the weight of said composition, of a member selected from the group consisting of



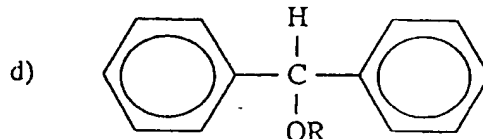
wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative and n is 0 or 1,



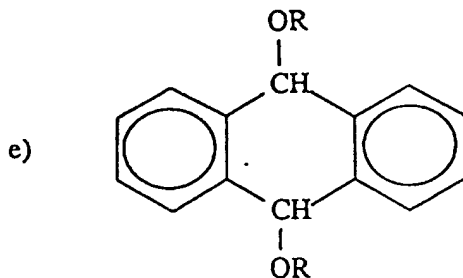
wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



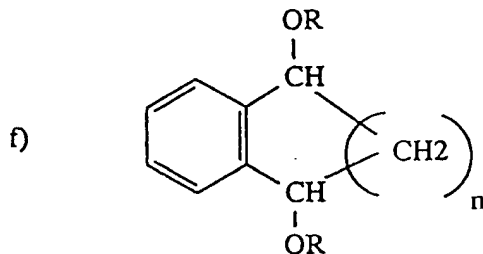
wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative,



wherein R denotes an alkyl or an aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative, and



wherein R denotes an alkyl or aryl radical having 1 to 30 carbon atoms or a dihydropyran derivative and n is 1 to 3.

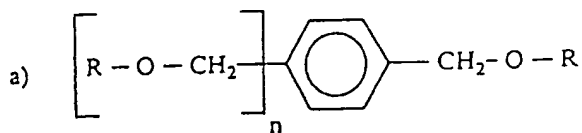
2. The molding composition of Claim 1 wherein said stabilizing amount is about 0.01 to 1.0 percent relative to the weight of said composition.

3. A molded article prepared from the composition of Claim 1.

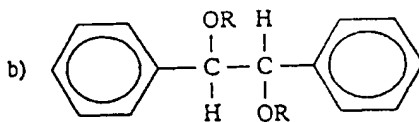
Patentansprüche

1. Polycarbonat-Formmasse, umfassend ein homogenes Gemisch aus
(i) einem aromatischen Polycarbonat-Harz und

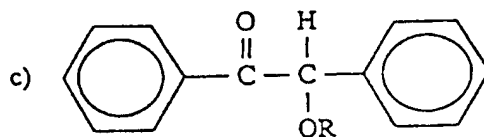
(ii) 0,01 bis 5,0 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, einer Komponente, die aus der aus



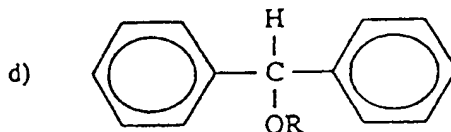
worin R einen Alkyl- oder Aryl-Rest mit 1 bis 30 Kohlenstoff-Atomen oder ein Dihydropyran-Derivat bezeichnet und n 0 oder 1 ist,



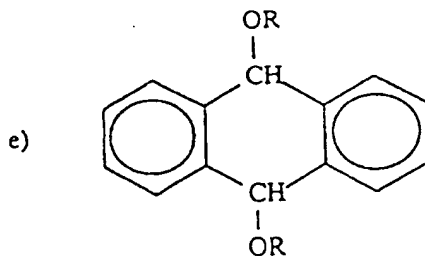
worin R einen Alkyl- oder Aryl-Rest mit 1 bis 30 Kohlenstoff-Atomen oder ein Dihydropyran-Derivat bezeichnet,



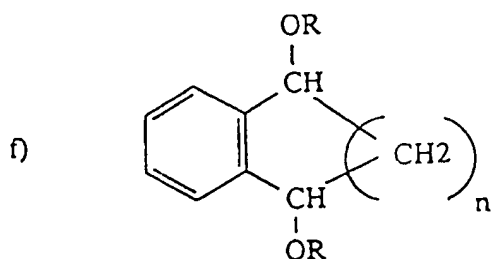
worin R einen Alkyl- oder Aryl-Rest mit 1 bis 30 Kohlenstoff-Atomen oder ein Dihydropyran-Derivat bezeichnet,



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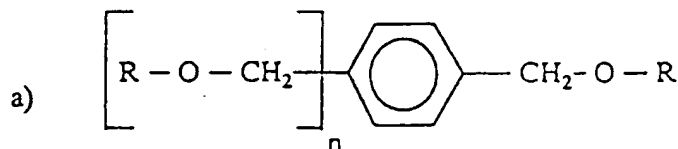


worin R einen Alkyl- oder Aryl-Rest mit 1 bis 30 Kohlenstoff-Atomen oder ein Dihydropyran-Derivat ist und n 1 bis 3 ist, bestehenden Gruppe ausgewählt ist.

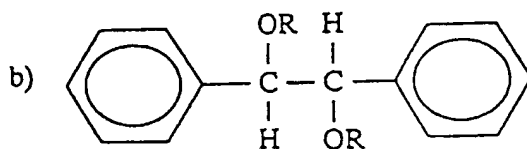
2. Formmasse nach Anspruch 1, worin die stabilisierende Menge etwa 0,01 bis 1,0 Gew.-%, bezogen auf das Gewicht der Zusammensetzung, beträgt.
3. Geformter Gegenstand, hergestellt aus der Masse gemäß Anspruch 1.

Revendications

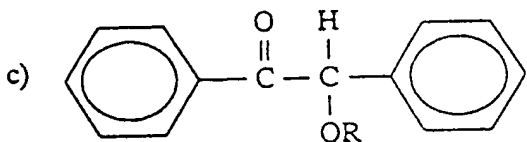
1. Composition de moulage de polycarbonate comprenant un mélange homogène
 - (i) de résine de polycarbonate aromatique et
 - (ii) de 0,01 à 5,0 %, basés sur le poids de ladite composition, d'un élément choisi parmi



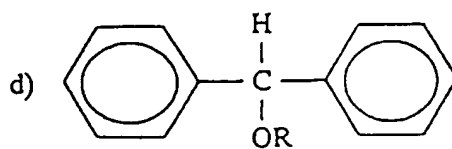
dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane et n est égal à 0 ou à 1,



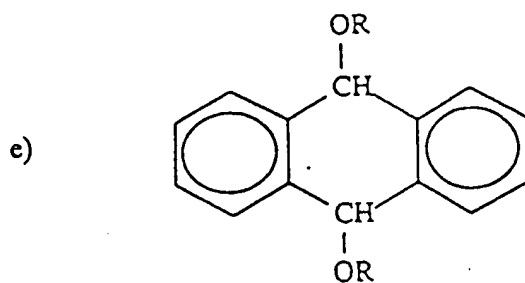
dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane,



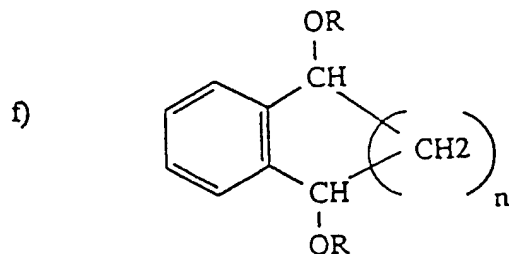
dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane,



dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane,



dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane, et



dans lequel R représente un groupe alkyle ou aryle en C₁-C₃₀ ou un dérivé de dihydropyrane et n est un nombre entier de 1 à 3.

2. Composition de moulage selon la revendication 1, dans laquelle ladite quantité de stabilisant est d'environ 0,01 à 1,0 %, basés sur le poids de ladite composition.

3. Article moulé préparé à partir de la composition de la revendication 1.